
Chapter 1

Cement Hydration

CEMENT HYDRATION

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1. INTRODUCTION

The term cement hydration applies to all the reactions of cement with water. These reactions determine to a great extent the concrete properties, as it is finally the mixture of cement with water which is the binding agent in concrete. With regard to the cement application, it is thus essential to have a basic understanding of the processes occurring during cement hydration.

To a minor extent, hydration reactions can also take place before the cement is applied in concrete during the storage of clinker and the grinding and storage of cement. Even this minor surface hydration may cause serious changes of the physical properties of cement. Table 1 gives an idea of the possible hydration of cement from clinker storage up to cement application.

Table 1: Occurrence of cement hydration

	Percentage hydration
Storage of clinker	0 to 10%
Grinding of cement	0 to 1%
Storage of cement	0 to 4%
Concrete mix	0 to 100%

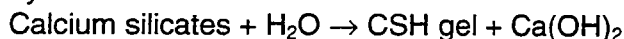
The study of the mechanisms and phenomena of cement hydration has a long tradition in cement research. First basic theories to explain setting and hardening of cement have been established by Le Châtelier and Michaelis at the end of the last century. The actual more refined theories still base on the work of these two researchers. The open questions remaining are principally related to the reaction of C_3S and C_3A at early stages.

2. MAIN FEATURES OF CEMENT HYDRATION

As for any chemical reaction, main features of interest with regard to the cement hydration are the hydration reactions, the mechanisms and kinetics and the heat of hydration. In the following, a brief overview on these three aspects shall be given:

◆ Hydration reactions

The nature of the hydration products is decisive for the mechanical properties of the hardened concrete. In Portland cement, the hydration is predominantly a reaction of the calcium silicates with water, producing a gel-like calcium silicate hydrate and calcium hydroxide:



In blended cements, the reaction schemes get more complex. Nevertheless, the hydration products are in general quite similar.

◆ Mechanisms and kinetics

The understanding of the mechanisms of cement hydration gives valuable indications on the reaction behaviour to be expected, including the kinetics. The knowledge of the kinetics of cement hydration and the influencing factors is very important for the concrete practice. The reaction speed of the cement hydration must be slow enough to allow the placement of concrete; after that, a rapid reaction is desired.

♦ Heat of hydration

The heat liberated during cement hydration may improve or impair the quality of the concrete. For ordinary Portland cement, the heat of hydration is typically 380 J/g at 28 days. This value is lower for the other special Portland cements with the exception of rapid hardening cement. In case of the blended cements, generally less heat is developed.

Besides the above mentioned chemical aspects, considerable changes in the physical properties of the cement are associated with the cement hydration. The principal changes are:

♦ Development of strength

From the practical point of view of course the most important change. As long as the hydration proceeds, the cement is continuously gaining strength.

♦ Increase in specific surface

The transformation of the low surface cement to a gel-like hydrated product of extremely high surface is one of the most striking changes of cement hydration. After complete hydration, typically a 1000 fold increase in specific surface is obtained.

♦ Increase in solid volume

The total volume occupied by the hydration products is roughly twice the volume occupied originally by the unhydrated cement. That means that 1 cm³ of cement will give more or less 2 cm³ of hydrated cement.

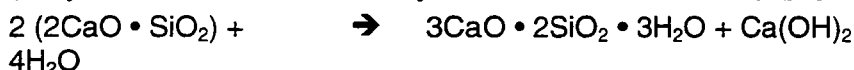
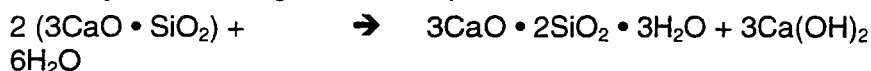
More detailed and specific indications on the different aspects of cement hydration will be given in the following chapters.

3. HYDRATION REACTIONS

3.1 Hydration of the individual clinker components

3.1.1 Calcium silicates

The hydration reactions of the two calcium silicates in clinker - C₃S and C₂S - can be represented by the following chemical equations:



The reactions of both silicates are thus stoichiometrically very similar and require more or less the same amount of water. The main difference between the two reactions is that C₃S produces more than twice as much calcium hydroxide as C₂S.

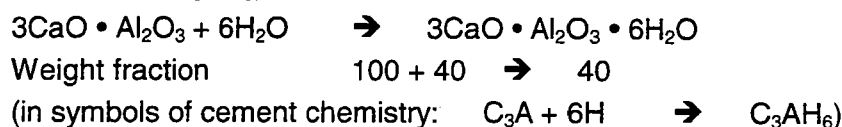
The principal hydration product of the calcium silicates is a gel-like or microcrystalline calcium silicate hydrate. The formula C₃S₂H₃ is only approximate, because the composition of this hydrate is actually variable over quite a wide range. In contrast, the calcium hydroxide formed is a crystalline material with a fixed composition.

It is believed that calcium hydroxide is not significantly contributing to strength and that the calcium silicate hydrates are in the first place responsible for the strength development. The

importance of the calcium hydroxide being a strong base is mainly related to its effects on the passivation of the steel reinforcement, the leaching of concrete and the reaction with reactive silica and alumina from pozzolanic additives.

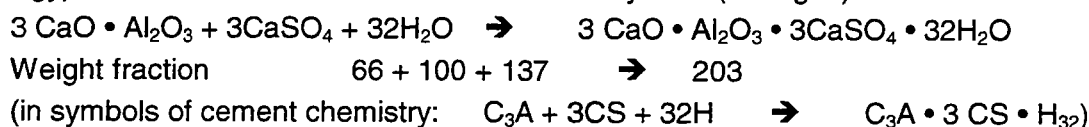
3.1.2 Tricalciumaluminate

The hydration of aluminates is heavily influenced by the presence of gypsum. In the absence of gypsum, the reaction of C_3A with water is very violent and leads to immediate stiffening of the paste (known as flash set) due to the rapid formation of hexagonal calcium aluminate hydrates (C_2AH_8 and C_4AH_{13}). These hydrates are not stable and later convert into the cubic form C_3AH_6 , so that the final form of reaction can be written as follows:

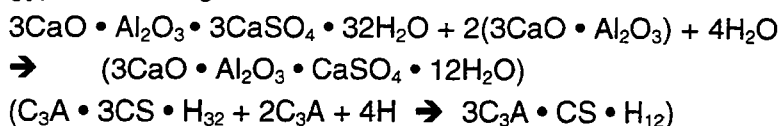


The theoretical capacity of C_3A to combine with water is such that 100 parts by weight of C_3A combine with 40 parts by weight of H_2O ; it is thus nearly double that of the silicates.

When gypsum is present in the cement, flash set can be avoided and the C_3A reacts first with the gypsum to form calcium trisulfate-aluminate hydrate (ettringite):



This reaction continues until all the available gypsum is used up. After the depletion of gypsum, ettringite is converted into the monosulfate:



Calcium aluminate hydrate continues to be formed from any remaining unhydrated C_3A and the final product of C_3A hydration is generally a monosulphate-calciumaluminate hydrate solid solution.

3.1.3 Ferrite phase

The C_4AF forms the same sequence of hydration products as does C_3A , with or without gypsum. The reactions are, however, slower; C_4AF never hydrates rapidly enough to cause flash set and gypsum retards C_4AF hydration more drastically than it does C_3A .

3.1.4 Calcium oxide and magnesium oxide

The uncombined lime (calcium oxide) and periclase (magnesium oxide), if present in large quantities in cement, may cause expansion due to a slow hydration reaction after the setting:



The actual degree of expansion depends on the state and distribution of these oxides in cement, in particular the large crystals of periclase or hard burnt free lime produce unsoundness.

3.1.5 Alkalis

Alkalis are present as alkalis sulphates or are incorporated in the main clinker phases. The first type of alkalis go readily into solution upon mixing with water and accelerate the early hydration reactions. The effect of alkalis contained in the clinker phases is not well known;

there is at least some dissolution with time which has some effect on later hydration reactions.

The presence of alkalis in the pore solution generally does not give any special problems except when certain aggregates are used that can participate in the alkali-aggregate reaction leading to expansion and disruption of the concrete. The aggregates giving rise to such a reaction contain either reactive silica or dolomite minerals.

3.2 Mineral additives

3.2.1 Blast furnace slag

Granulated blast furnace slag does not hydrate per se in water, but in the presence of activators like lime, alkalis, sulphate and Portland cement, it shows hydraulic properties. The activators appear to function by the removal of passive surface films that act as a barrier to significant hydration. The glass in the granulated slag is the hydraulic component in the presence of Portland cement.

The hydration reactions of blast furnace slag are not easy to follow and it is thus difficult to establish clear reaction equations. Studies on slag cements have revealed that the hydration products of the slag hydration are similar to those of the calcium silicate reaction. It is believed that the main difference to Portland cement hydration is the lower C/S ratio of the calcium silicate hydrates and the reduced amount of calcium hydroxide present.

3.2.2 Pozzolanic additives

The natural and artificial pozzolans contain reactive siliceous and aluminous materials which on their own do not possess cementitious properties. They react, however, in the presence of water with dissolved calcium hydroxide released from the hydration of the Portland cement clinker. The reaction products are calcium silicate and calcium aluminate hydrates similar to those found in the hydration of Portland cement clinker. Favourable for this pozzolanic reaction seems to be the presence of alkalis.

3.2.3 Limestone filler

Finely ground limestone can react during hydration with the C_3A from the clinker to form monocarboaluminate ($C_3A \cdot CaCO_3 \cdot 11H_2O$). The presence of limestone in the cement can thus to a certain extent retard the hydration of C_3A , but it is by far less effective than gypsum and can not avoid flash set. Moreover, fine limestone filler can have an indirect influence on the hydration reaction of C_3S .

4. MECHANISM AND KINETICS

4.1 Basic theories

As mentioned in the introduction, the first theories to explain setting and hardening of cement were advanced by Le Châtelier and Michaelis. Le Châtelier attributed the development of cementing action to the passage of the anhydrous cement compounds into solution and the precipitation of the hydration products as interlocking crystals. In the theory put forward by Michaelis, cohesion is considered to be the result of the formation of a colloidal gelatinous mass. The formation of the gel may take place without the cement compounds going into solution by a direct „topochemical“ or „solid state“ reaction.

Both hydration mechanisms take place within in the cement paste. Cementitious reaction initially takes place by some dissolution and precipitation, whilst the hydrated material formed has only a small degree of crystalline order being gel-like and of colloidal dimensions. The colloidal theory can also explain the phenomena of swelling, shrinkage, creep and selfhealing of cracks.

4.2 Reaction sequence during cement hydration

Hydration of cement is a sequence of overlapping chemical reactions between clinker components, mineral additives, calcium sulphate and water, leading to continuous cement paste stiffening and hardening. The hydration reactions described before proceed simultaneously at differing rates and influence each other.

A simplified schematic presentation of the hydration process of Portland cement is given in Figure 1. The three main stages which can be distinguished in this presentation are:

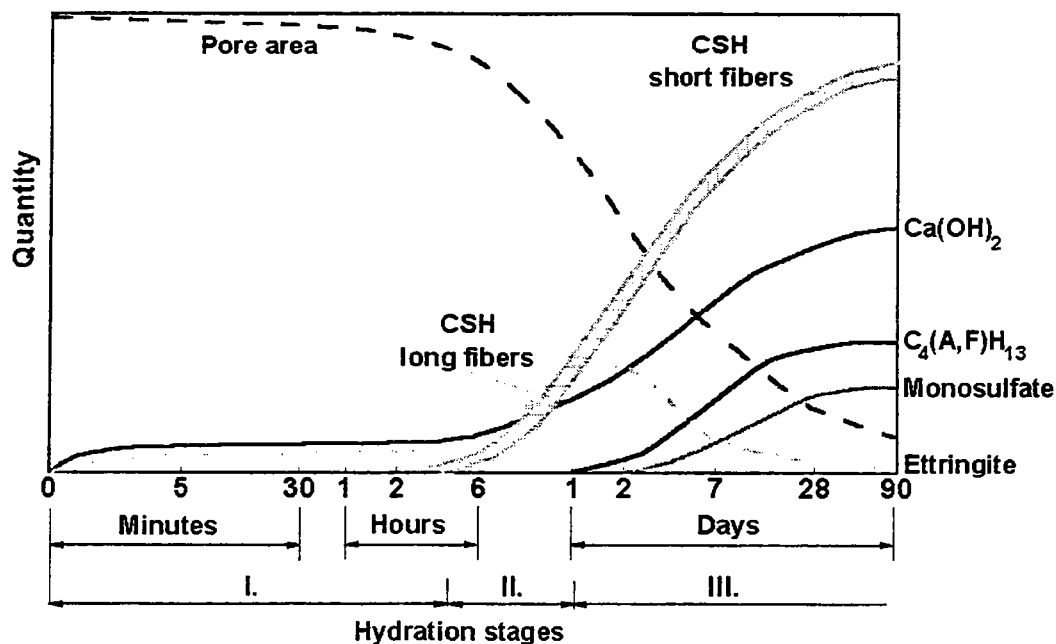
First stage

In the first stage, ettringite and calcium hydroxide are formed. The ettringite covers the aluminate particles and avoids flash set of the cement paste. After these first reactions, the so-called „dormant“ period of typically four to six hours starts where no considerable further hydration takes place (certain increase in Ca^{2+} concentration).

The dormant period is usually explained by the behaviour of the C_3S , the main constituent of Portland cement. The two principal theories are based on the protective layer and the delayed nucleation concept respectively. The first ascribes the „dormant“ period to the formation of a protective layer on the C_3S particles which is destroyed with time and the latter regards the retardation in C_3S reaction as the cause of a delayed nucleation of the corresponding hydration phases.

Still in the first stage, the cement paste is setting. This stiffening is attributed by some researchers to the recrystallisation of the initially finely divided ettringite. Others believe that the setting is caused by the loss in plasticity due to some first formation of calcium silicate hydrate from C_3S .

Figure 1: Schematic representation of the formation of hydrate phases in Portland cement paste



Second stage

The second stage after the dormant period is characterised by the restarting of the hydration. Precipitation of CSH in form of long fibres and calcium hydroxide takes place on the surface of the silicate phases and the reaction proceeds rapidly for all clinker phases. This stage ends with the termination of the ettringite formation and the development of a basic matrix after about 24 hours.

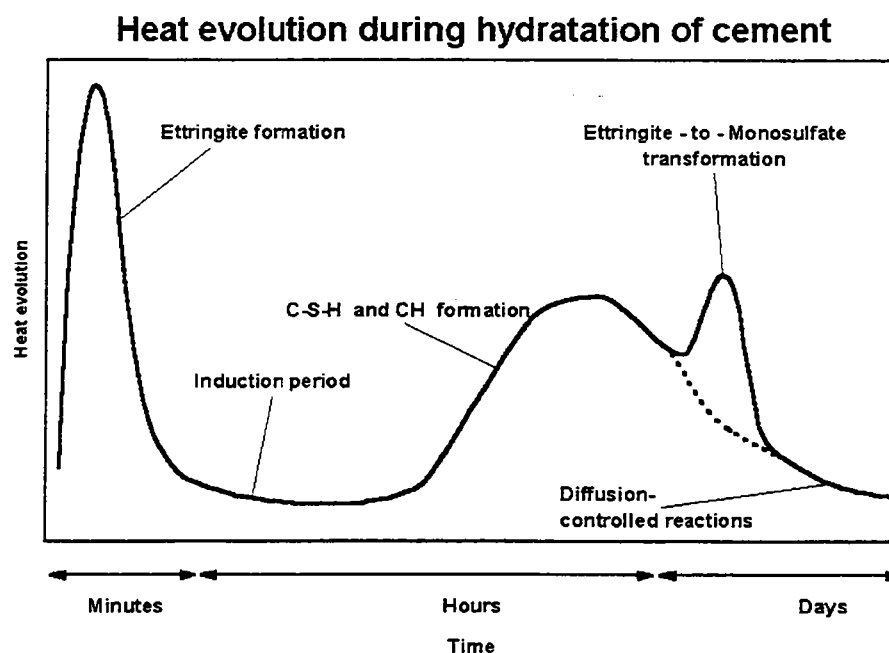
Third stage

In the third stage, the spaces between the solid particles are overbridged and filled with short fibres of the CSH phase. The initial matrix, formed by first hydrates of the aluminate, ferrite and silicates, is thus densified and the strength of the cement paste increases. The calcium hydroxide formed in large crystals is built into the CSH gel matrix. At this stage, ettringite is converted into monosulfate and corresponding hydration products are formed from the still not hydrated aluminate and ferrite phases.

As the hydration proceeds, the reactions get more and more diffusion controlled and the overall rate of reaction is decreasing. Hydration reactions, primarily those of C_2S , will continue as long as the reactants and space permit it; this can go on for years. In practice, there is usually never a complete hydration of the cement and unhydrated cement is nearly always remaining in the hardened cement paste.

A good overview on the hydration reactions in Portland cements can also be obtained by taking a look at the heat evolution curves. Figure 2 shows such a curve with the indications of the main reactions going on in the process of cement hydration.

Figure 2: Heat evolution curve of Portland cement



For blended cements, the reactions sequences get more complex. In case of the active mineral additives, the main differences to Portland cement hydration can be seen in more formation of CSH phase at later stage and a decrease in the amount of calcium hydroxide and the pore space. For the inert mineral additives, the effect will primarily be a „dilution“ of the Portland cement matrix.

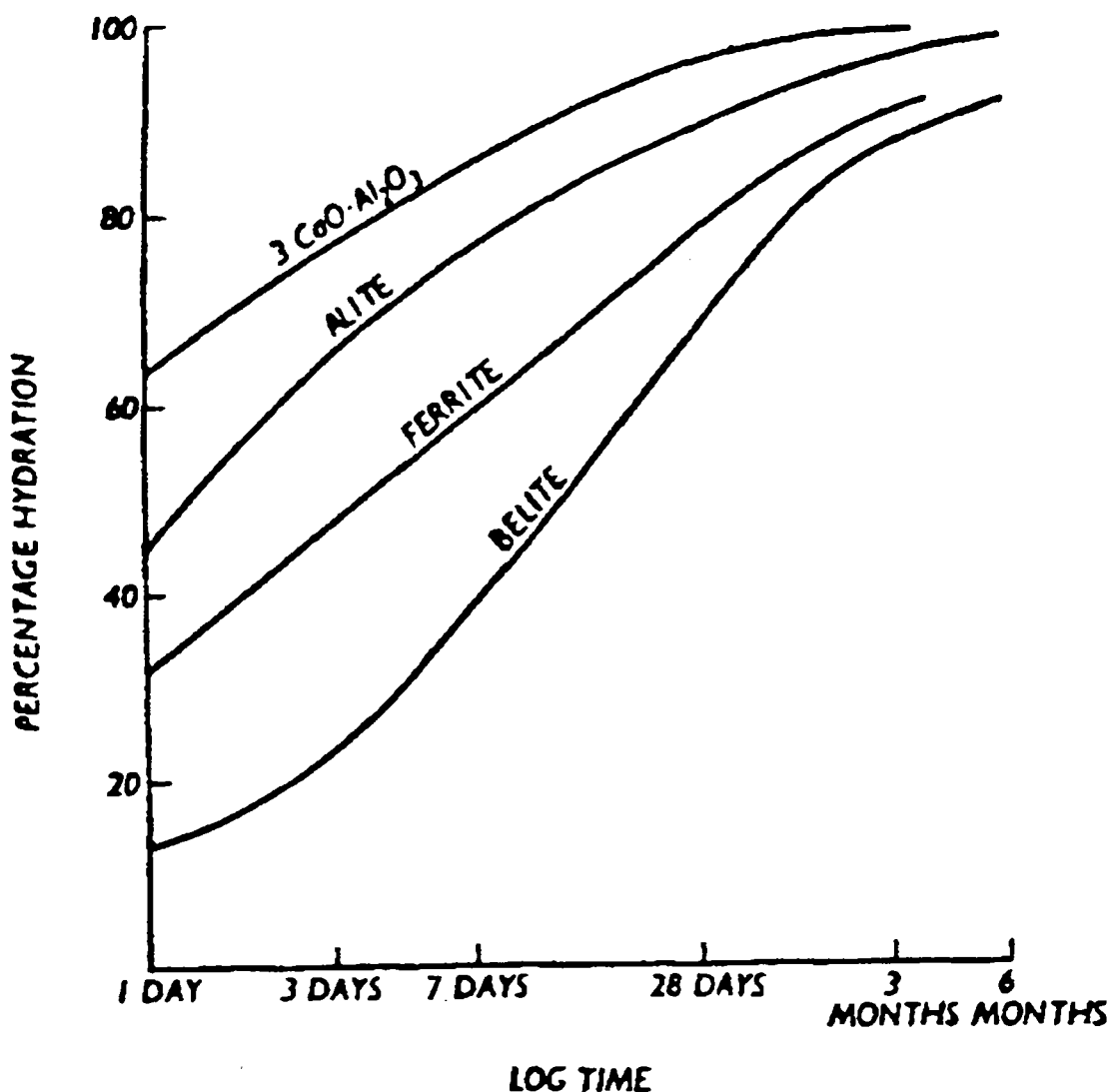
A general effect observed in blended cement is a certain delay of setting and hardening at early stages. Normally, the active mineral additives start to contribute to cement hydration only after more than 3 days, when suitable activation has taken place (blast furnace slag) or sufficient calcium hydroxide has been formed (pozzolans) for their reaction.

4.3 Acceleration or retardation of cement hydration

The process of hydration can be accelerated or retarded by different factors:

- ◆ **Use of accelerators and retarders**
Until now, the most efficient accelerator is calcium chloride (CaCl_2), but the problem with this product is the corrosion of the steel reinforcement. The exact mechanism of acceleration by CaCl_2 is not known; it is believed that CaCl_2 is acting like a catalysator. Retarders for cement hydration are for instance phosphates, zincates and carbohydrates (including sugar). The retarding action is simply explained by the formation of a monomolecular protective film around the cement particles which slows down their reaction with water.
- ◆ **Hydration temperature**
The rate of hydration is strongly influenced by the temperature. Rate of hydration at early age roughly doubles when the temperature increases by 10°C . The effect of temperature on cement hydration is of particular importance in extreme climates and for steam curing.
- ◆ **Cement fineness**
The higher the fineness of the cement, the more extended is the zone of reaction. This leads of course to a higher rate of hydration.
- ◆ **Cement composition**
The activity of the clinker used in the cement affects considerably the rate of hydration. A high rate of hydration can be expected of clinkers rich in C_3A and C_3S (see Figure 3) and with a high alkali content.
Important for the rate of hydration is also the content of mineral additives in the cement. The rate of hydration generally is the lower, the higher the dosage of mineral additives in the cement.

Figure 3: Rates of hydration of compounds in Portland cement

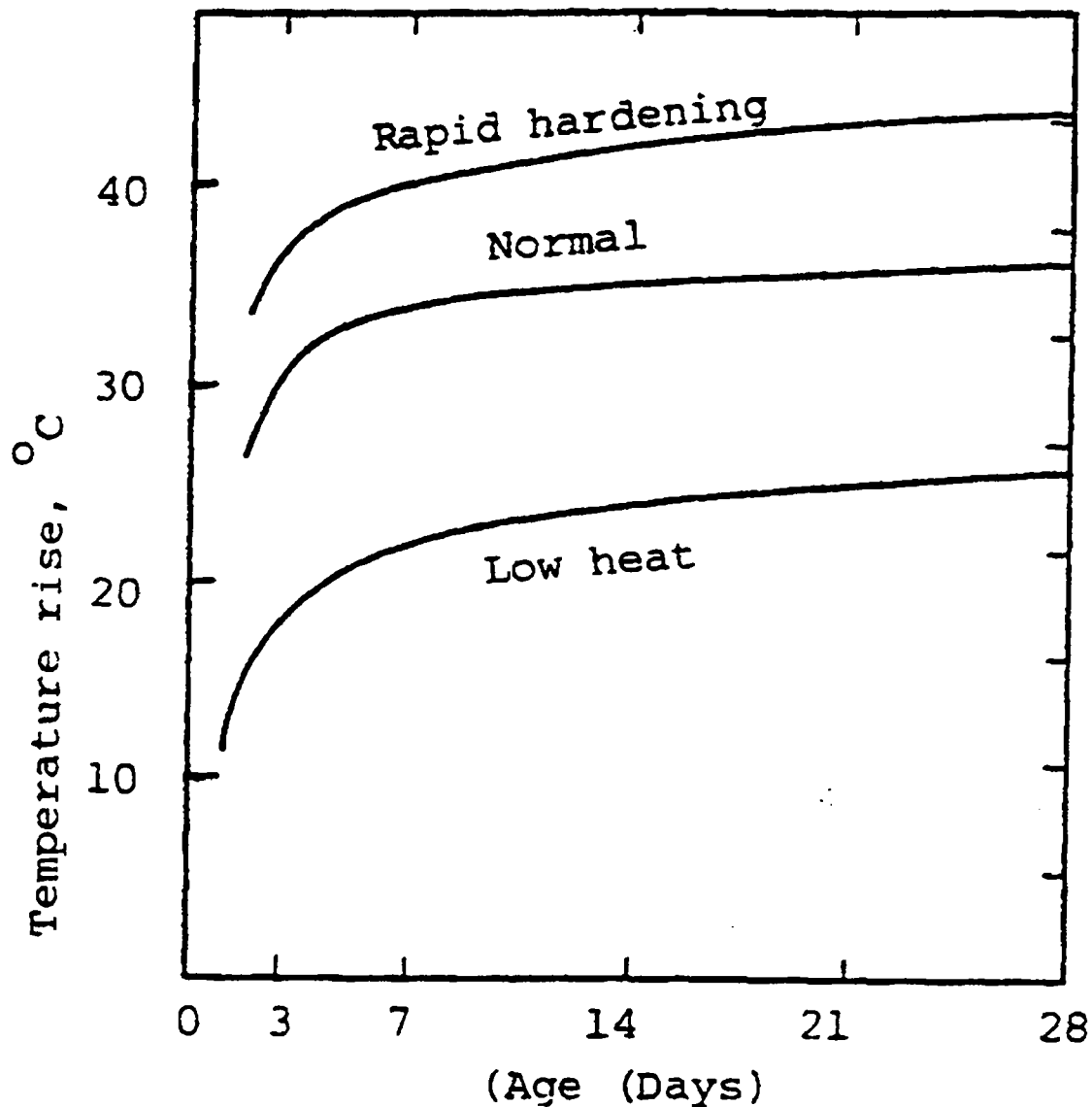


Increasing the rate of hydration, and hence the early strength development, is always done at the expense of the ultimate strength. An explanation is that the microstructure formed during the accelerated hydration is usually more coarse and less favourable for strength development. Contrary to this, retarded, slow hydration leads to the formation of a more refined microstructure which results in better final strength.

5. HEAT OF HYDRATION

The hydration reaction is an exothermic process, that means during the reaction of cement with water heat is liberated. The quantity of liberated heat is quite appreciable (typically 380 J/g for OPC at 28 days) and can lead to a significant temperature rise in mass concrete construction, where the heat is not allowed to escape (see Figure 4). During cooling of the hardened concrete, thermal gradients may develop and give problems with crack formation. That is the reason why special low heat cements have to be used for mass concrete applications.

Figure 4: Temperature rise in 1:9 (weight) concrete under adiabatic conditions for different Portland cement types



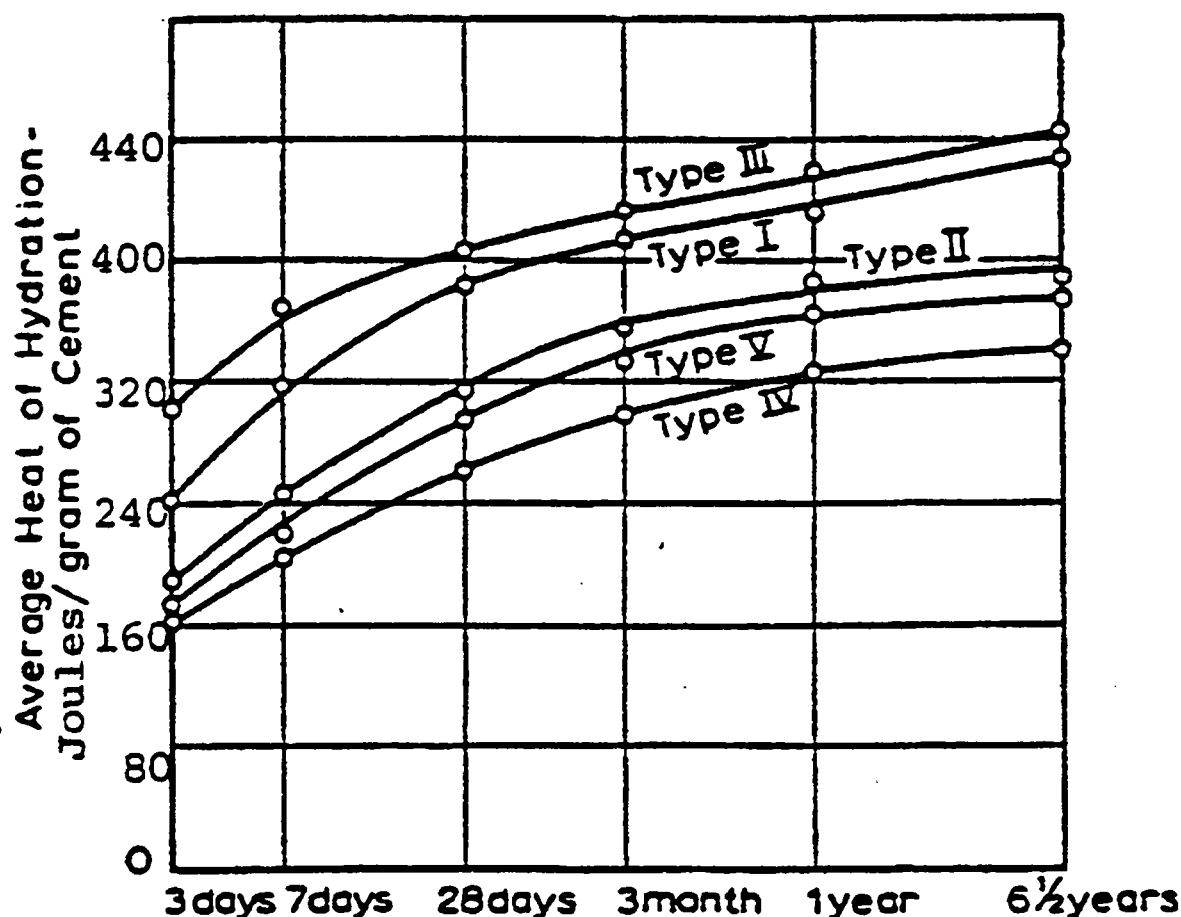
The main measure to control the heat of hydration of Portland cement is the adjustment of clinker composition. The clinker minerals contributing most to the heat of hydration are C_3S and C_3A (see Table 2), so that it is necessary to limit these compounds to reduce heat development during hydration. On the other hand, it is also possible to keep the heat liberation low by not grinding the cement too fine.

Table 2: Heat of hydration of the clinker components at 21°C (J/g)

Clinker component	3 days	28 days	6 ½ years
C ₃ S	245	380	490
C ₂ S	50	105	225
C ₃ A	890	1380	1380
C ₄ AF	290	495	495

The effect of clinker composition and cement fineness on the heat of hydration can be well seen in Figure 5 which shows the development of heat of hydration for the different Portland cement types. The low heat cements used for mass concrete - type II and IV ASTM - with low heat of hydration of about 250 to 300 J/g after 28 days contain less C₃S and C₃A and are fairly coarse. The rapid hardening cement - type III ASTM - with increased heat of hydration of about 420 J/g after 28 days is usually richer in C₃S and C₃A and of higher fineness, compared with the ordinary Portland cement - type I ASTM.

Figure 5: Development of heat of hydration for the different Portland cement types cured at 21°C (w/c-ratio of 0.40)



For practical purposes, it is not only the total heat of hydration that matters but also the rate of heat evolution. The same total heat produced over a long period of time can be dissipated to a greater degree, consequently producing a smaller rise in temperature in the concrete. In ordinary Portland cement about one half of the total heat is liberated between 1 and 3 days and about three quarters in 7 days. It is common to specify the heat of hydration after 7 and 28 days, giving a reasonable indication of both total heat of hydration and its rate of liberation.

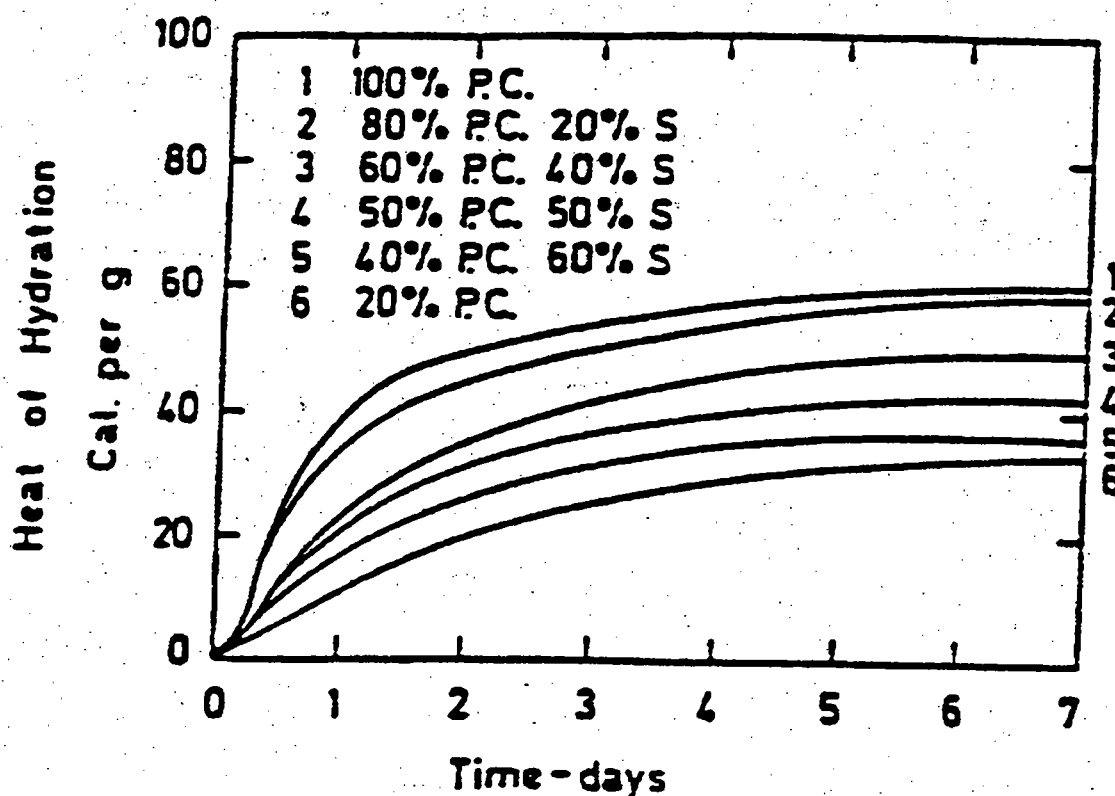
In addition to the composition and fineness of cement, the rate of heat evolution is also greatly influenced also by the temperature of hydration (see Table 3). The ambient conditions thus play also a decisive role with regard to the effects of heat of hydration on the concrete properties.

Table 3: Heat of hydration (J/g) developed after 3 days at different temperatures

Cement type	Temperature of cement hydration			
	4°C	24°C	32°C	41°C
I	154	285	309	335
III	221	348	357	390
IV	108	195	192	214

A very effective means to reduce the amount and rate of heat of hydration of Portland cement is the use of mineral additives in the cement (blended cements). By the replacement of the clinker by the less reactive or inert mineral additives, the heat development of the cement can be easily controlled. As an example, the heat development curves of slag blends with different Portland cement contents are presented in Figure 6. The advantage of the blended cement over the low heat Portland cements is that the same clinker as for the ordinary Portland cement can be used.

Figure 6: Heat of hydration of mixtures of OPC (P.C.) and ground blast furnace slag (S); isothermal method.



6. ROLE OF GYPSUM IN CEMENT

6.1 General aspects

Ever since cement has been produced in greater quantities, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has been ground into the cement. Gypsum is added to the cement mainly for the purpose of regulating its setting time. It prevents flash setting and makes the concrete workable for hours.

The gypsum influences not only the setting but also other cement properties such as grindability, sensitivity to storage, volume stability and strength. Gypsum is an extremely important part of cement. It is, however, often neglected to pay proper attention to it in the production of cement.

Here, only the effect of gypsum on setting, volume stability and strength shall be elucidated more in detail. For the better understanding of the influence of gypsum on cement, it is first necessary to take a look at the different modifications in which calcium sulphate can be present. In a final part of this chapter, the possible gypsum substitutes shall be discussed.

6.2 Calcium sulphate modifications

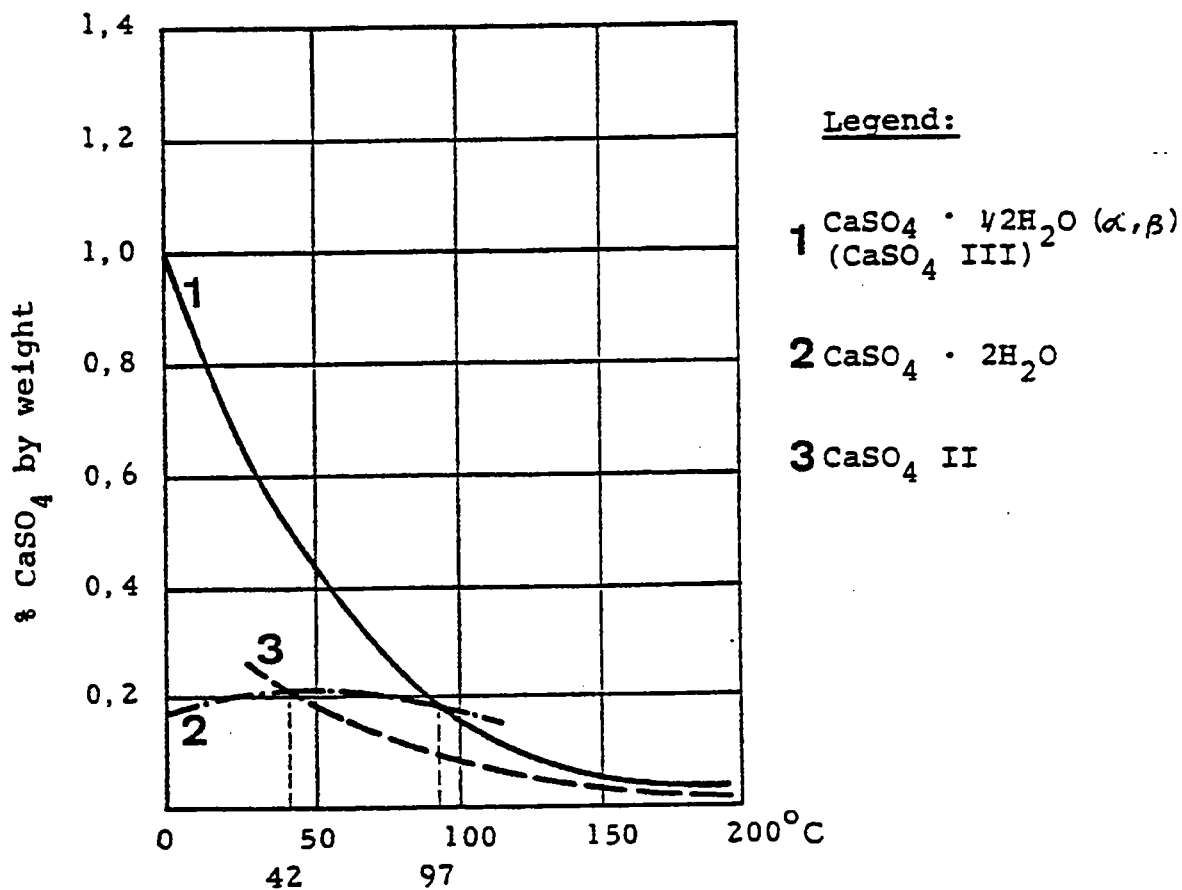
In cement, it is possible to find at least five basic modifications of calcium sulphate (see Table 4). The stable modifications, dihydrate (gypsum) and anhydrite II (natural anhydrite), can be found in nature and both are used as additives to clinker in the grinding process. The metastable modifications, hemihydrate and anhydrite III, are not available in nature, but can easily form during grinding and storage of cement at elevated temperatures by dehydration of gypsum. The high temperature modification anhydrite I can form during burning of the clinker in the cement kiln.

Table 4: Modifications of calcium sulphate in cement

Designation	Formula	Crystal water %	Density g/cm^3	Range of stability $^{\circ}\text{C}$	Solubility at 20°C %	Occurrence	
						nature	cement
Dihydrate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	20.92	2.32	< 40	0.20	yes	yes
Hemihydrate (α, β)	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	6.21	2.70	metast.	0.95	no	yes
Anhydrite III (α, β)	CaSO_4	0	2.50	metast.	0.95	no	yes
Anhydrite II	CaSO_4	0	2.98	40-1180	0.20	yes	yes
Anhydrite I	CaSO_4	0	--	> 1180	--	no	(-clinker)

The different mode of action of the individual modifications on the properties of cement can be mainly attributed to their different solubilities in water. In Figure 7, it can be seen that the solubility of the hemihydrate and anhydrite III is appreciably higher than that of dihydrate or anhydrite II. The high solubility of hemihydrate and anhydrite III can lead to anomalous setting, as discussed later. The solubility of dihydrate and anhydrite II in the ambient temperature range is approximately the same, but their effect on properties of cement can be very different. The reason for this is the different rate of solubility which is greater for the dihydrate than for anhydrite II.

Figure 7: The Solubility of gypsum, hemihydrate and anhydrite

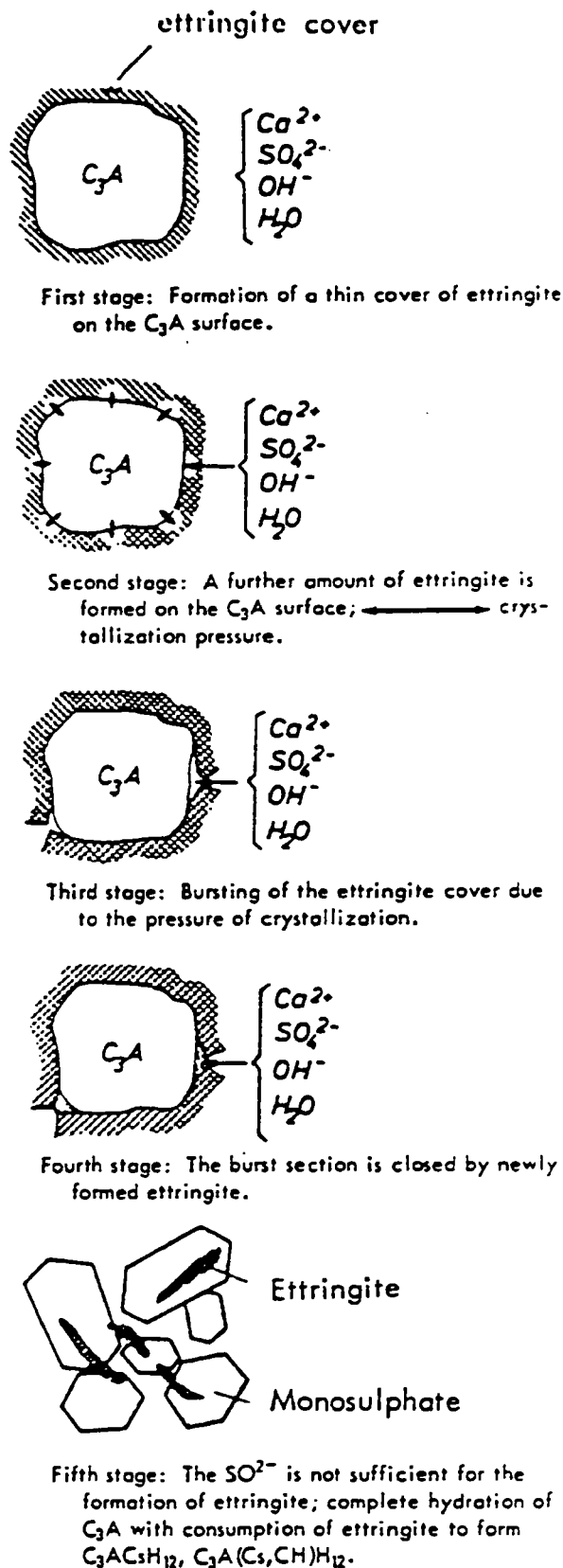


6.3 Gypsum and setting of cement

The reactions which take place immediately after the addition of water to cement are of decisive importance for the setting of cement. Directly after the mixing of cement with water, sulphate dissolves and reacts with aluminate to form ettringite. This vigorous initial reaction ceases after a few minutes and then the so-called dormant period starts.

According to the classical theory, the set retardation is due to the fact that the ettringite forms a cohesive cover around the aluminate particles and in this way inhibits their further reaction (see Figure 8). The reaction inhibiting effect of the ettringite cover is ended only when this cover is broken open by the pressure of crystallisation and not sufficient sulphate is left to close the burst section. Thereafter, the reaction of C_3A can continue unhindered until complete hydration.

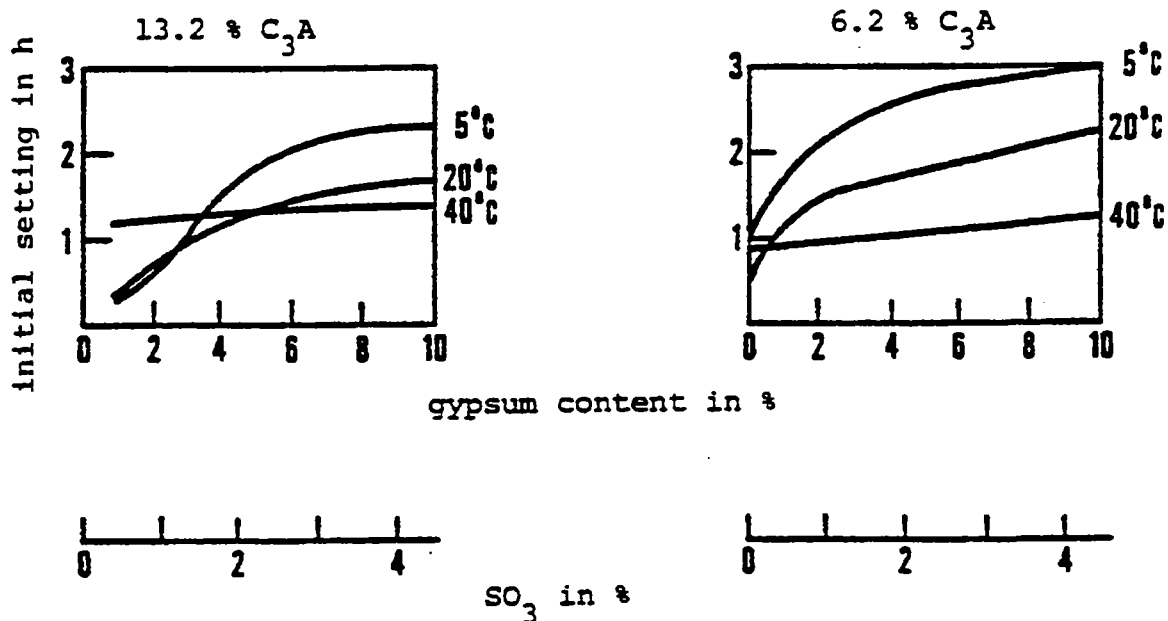
Figure 8: Schematic description of set retardation due to C_3A sulfate interaction



The reasons for the setting of cement are still not exactly known. Some researchers explain the setting of the cement by the recrystallisation of the initially finely divided ettringite into bigger crystals which are building bridges between the cement particles. Other researchers attribute the initial set of cement as corresponding to that stage in the hydration sequence when a sufficient amount of tricalcium silicate has been converted to calcium silicate hydrate. This initial removal of water causes a partial loss of the plasticity of the cement paste.

The setting of cement is mainly influenced by the reactivity of the clinker (i.e. C_3A and alkali content) and by the type and amount of the calcium sulphate added. The cement fineness, the dosage of mineral additives, use of chemical admixtures and the hydration temperature play also an important role. The effect of C_3A content, gypsum dosage and hydration temperature on the initial setting of Portland cement is illustrated in Figure 9.

Figure. 9: Influence of gypsum dosage, C_3A content and hydration temperature on initial setting of Portland cement



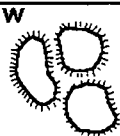
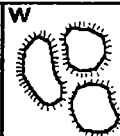
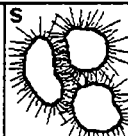
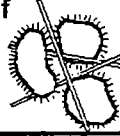
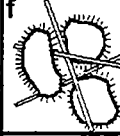
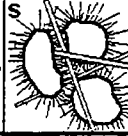
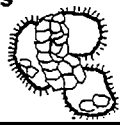
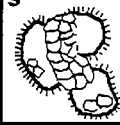
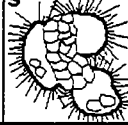
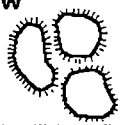
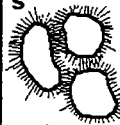
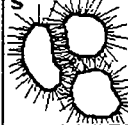
In order to obtain normal setting, it is essential to adjust the supply of soluble sulphate to the reactivity of the clinker during the first minutes and hours of hydration (see Figure 10). If there is no proper balance between sulphates and clinker reactivity, abnormal setting can occur:

Flash set is caused by the formation of aluminate hydrate, due to a high content of reactive C_3A and/or a too small amount of easily soluble calcium sulphate.

False set can be traced back to high temperature in the mill, causing a dehydration of the gypsum to an easily soluble hemihydrate and anhydrite III. Hemihydrate and anhydrite III recrystallize to gypsum whose crystals grow into each other and form a solid framework which affects the stiffening of the cement paste. This framework of gypsum crystals is broken down again through reaction with C_3A . For this reason the cement paste can regain its previous plasticity by remixing.

Quick set: The high content of easily soluble sulphate and reactive clinker minerals can also have an accelerating effect on the formation of sulfo-aluminate hydrate and calcium silicate hydrate which can likewise lead to early stiffening of the cement (quick set).

Figure 10: Formation of rigid structure during setting of Portland cement

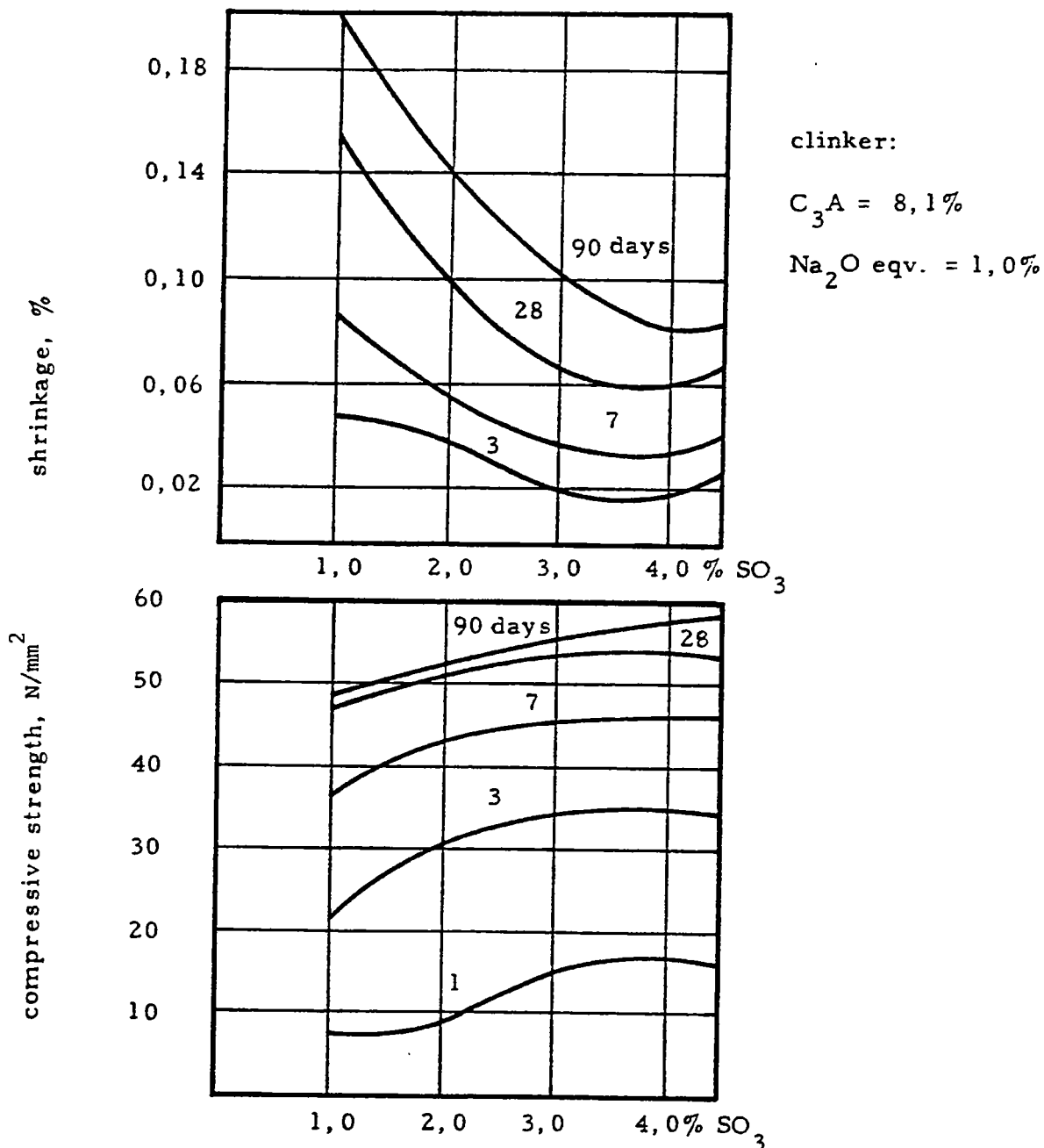
Clinker reactivity	Sulfate availability in solution	Type of set	Time of hydration		
			10 min.	1 hour	3 hours
low medium	low medium	regular			
low	high	false			
high	low	flash			
high	high	quick			

w = workable s = set f = false set

Effect of gypsum on strength and volume stability

The addition of gypsum - in addition to its principle purpose of regulating setting - has a significant effect on the strengths and volume stability. Up to a certain limit, which depends on the clinker composition, the gypsum addition increases the strengths and prevents shrinkage. If the gypsum addition surpasses this limit, it causes considerable swelling which can lead to expansion. This is why an upper limit for the SO_3 content is given in the cement standards (see Fig. 11).

Figure 11: Shrinkage and compressive strength of cements as a function of the SO₃ Content



The gypsum required to obtain optimum strength and volume stability grows with the C_3A content of the clinker, cement fineness, alkali content and application temperature. Other variables influencing the optimum SO₃ content are the form (and solubility) of the calcium sulphate in the cement, the nature and amount of mineral additives and also the presence of chemical admixtures. Often the optimum SO₃ content would be even above the maximum value given by the standards.

6.4 Gypsum substitutes

There has never been lack of effort to substitute gypsum by other set regulators. In particular in countries with few natural gypsum deposits, the cement industry is searching

intensively for alternative materials. The main alternatives up to date are the use of natural anhydrite and limestone and the application of by-product gypsum coming from other industries.

The use of natural anhydrite as partial substitute for gypsum is already well established in practice. In general, it appears that blends of 40 to 60 percent gypsum and 60 to 40 percent natural anhydrite can be safely used with all clinkers. The advantage of such blends over pure gypsum is the reduction of the risk of false setting and the improved storage stability and flowability of the cement.

In some places, limestone is used as replacement for gypsum. For very reactive clinkers, the replacement is typically limited to 25%. In cements with less reactive clinkers, replacement levels of up to 50% may be possible without negative effects on the setting of cement.

With respect to by-product gypsum, there are a number of commercial processes which produce such materials. An overview on the main sources of by-product gypsum is given in Table 5; the most important sources regarding quantities are phosphogypsum and desulfogypsum. Another type of by-product not mentioned in the table are used plaster moulds, which are for instance used in casting certain clay products.

Table 5: Main sources of by-product gypsum

Product/process	By-product	% sulphate*	% impurities
orthophosphoric acid	phosphogypsum	95-98 (G)	0.2-1.5 P ₂ O ₅ , up to 1.5 fluoride
hydrofluoric acid	fluorogypsum	80-95 (HH or AH)	2-3 CaF ₂ , unreacted silicofluorides
citric, formic and tartaric acid	organogypsum	---	---
boric acid	borogypsum	40-50 (G), 20-30 (AN)	7-10 H ₃ BO ₃
flue gas SO ₂ removal	desulfogypsum	90-95 (G), sulfite for mod. process	---
titanium white	titanogypsum	90-95 (G)	0.4 TiO ₂

* G = CaSO₄ • 2H₂O, HH = CaSO₄ • ½H₂O, AN = CaSO₄

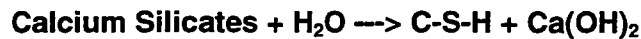
The main problem for the use of such by-products as substitute for natural gypsum is the presence of impurities, which may have some harmful effect on setting, strength development or some other property of the cements. Moreover, the amount of impurities can fluctuate quite a lot so that the variability in cement properties may also be higher.

7. MICROSTRUCTURE AND PROPERTIES OF HARDENED CEMENT PASTE

7.1 Basic physical features

In this section we deal with the physical structure of hydrated cement paste (HCP), as well as the effect of its morphology on the important properties of hardened concrete.

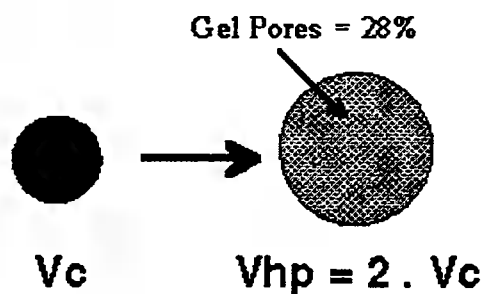
We will be concerned with the main chemical reaction taking place during hydration:



where C-S-H are the hydrates of the Calcium Silicates (C_3S and C_2S), also called "C-S-H gel".

The most important physical aspect of that reaction is the fact that the total volume occupied by the hydration products is, roughly, twice the volume occupied originally by the unhydrated cement (see Figure 12):

Figure 12: Basic physical feature of cement hydration

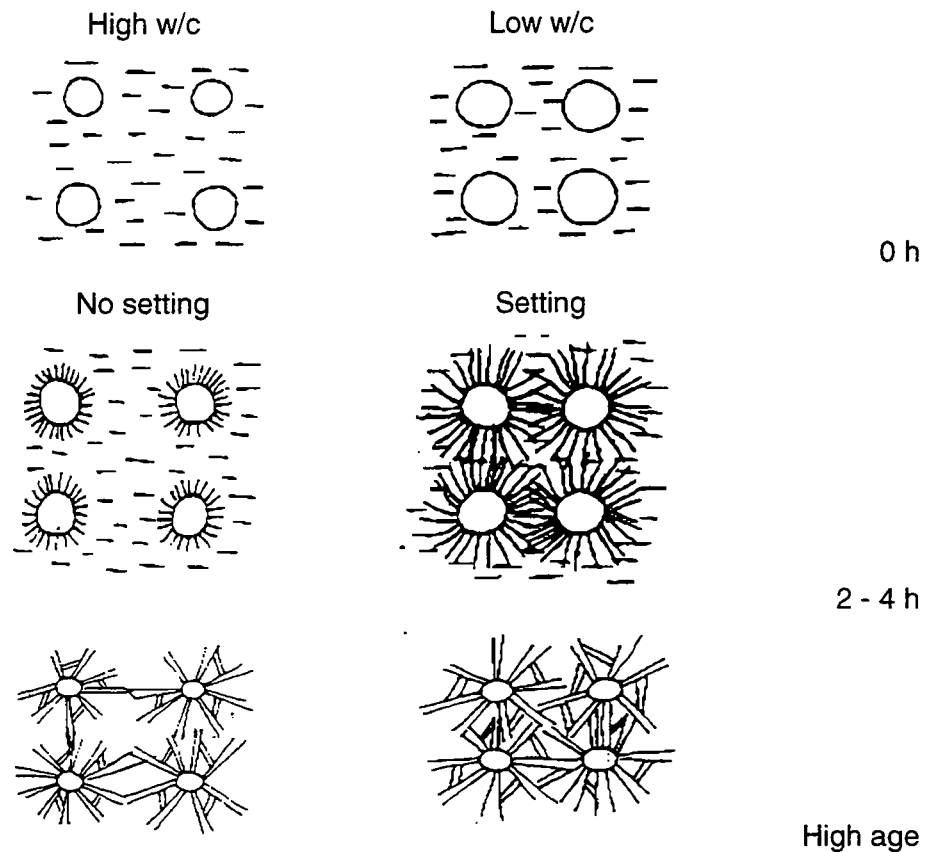


It must be mentioned that, out of that total volume, 28 % are very small pores (gel pores) and the rest (72 %) is solid phase:

$$\text{Gel pores} = 0.28 V_{hp}$$

Figure 13 shows schematically the growth of crystals during hydration of two pastes, one of low and the other of high water/cement ratio (w/c). The w/c ratio is a measure of the degree of dispersion of the cement grains in water.

Figure 13: Structure formation in cement paste during hydration



Cement hydration can be seen as a continuous process by which the capillary pores (space originally occupied by water) are being gradually filled with hydration products.

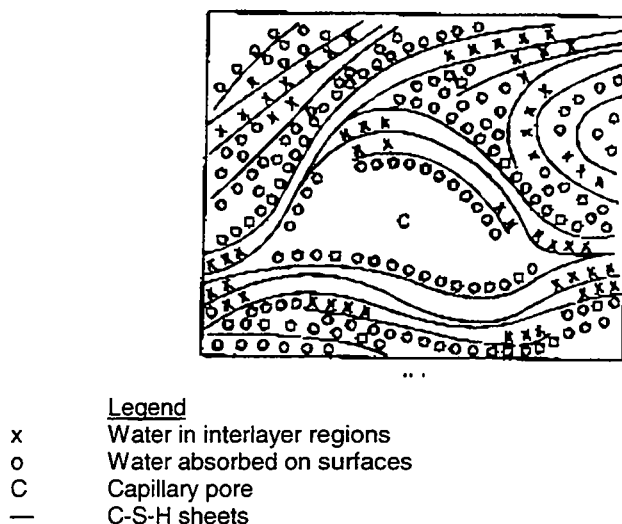
7.2 Morphological features

Figure 14 presents a model (Feldman and Sereda) of the general structure of HCP, showing its main features.

In the hydrated cement paste, there are two distinctive phases:

- ◆ Solid Phases
- ◆ Pores (at least partially filled with water)

Figure 14: Model of Feldmann and Sereda for the general structure of hydrated cement paste

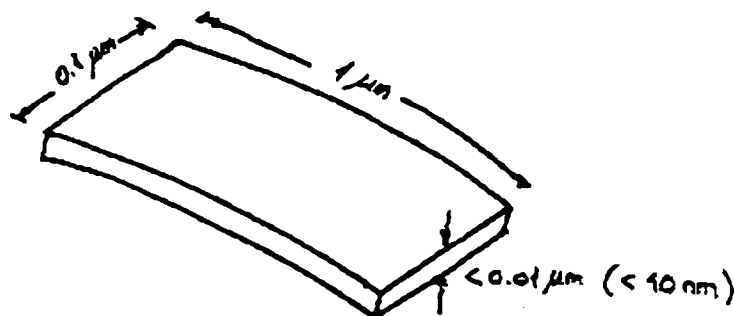


7.2.1 Solid phases

7.2.1.1 Calcium silicate hydrates-(C-S-H)

The C-S-H particles occupy 50 - 60 % of the total solid volume in hydrated paste; it is also called C-S-H gel. The particles are very small (colloidal dimensions) and sheet-like shaped (see Figure 15)

Figure 15: Basic feature of C-S-H particle



The C-S-H particles are arranged as a highly disordered layered structure (see Figure 14) with very high specific surface $\approx 3.000.000 \text{ cm}^2/\text{g}$.

The strength of the HCP is attributed to the attraction forces between the C-S-H crystals over their enormous surface.

The space left between the particles is called gel pores; these pores are extremely small (about 1.5 nm), of the order or magnitude of a water molecule (0.25 nm).

7.2.1.2 Calcium Hydroxide (CH)

Compound with a definite stoichiometry: $\text{Ca}(\text{OH})_2$, forming large crystals (0.01 - 0.1 mm) of hexagonal shape (Portlandite).

These crystals constitute 20 - 25 % of the solid volume in the hydrated paste.

Their contribution to strength is low (low surface area); however, their presence is very important to passivate the embedded steel rebars.

7.2.1.3 Calcium Sulfoaluminates

Occupy 15 - 20 % of solid volume in hydrated paste; they only play a minor role in strength.

There exist two forms:

Ettringite: Elongated needle shaped crystals

Monosulfate: Hexagonal plates or "rosettes"

Iron oxide can replace aluminium oxide in the Crystal structure.

7.2.1.4 Unhydrated Clinker Grains

Smaller grains react faster and coarser grains ($> 30 \mu\text{m}$) tend to remain partially unhydrated.

7.2.2 Pores

7.2.2.1 Interlayer space in C-S-H (gel pores)

Occupy 28 % of bulk volume of C-S-H gel

Size: 0.5 nm - 2.5 nm (H_2O molecule = 0.25 nm)

They are always present in HCP but, due to their small size do not adversely affect strength and permeability. However, the movement of water - that is firmly held within the gel pores - is the main reason for drying shrinkage and creep.

7.2.2.2 Capillary pores

Represent the space originally occupied by water, not filled with hydration products. Their size and volume depend on the w/c ratio and the degree of hydration:

- ◆ well hydrated paste, low w/c: 10 - 50 nm
- ◆ at early ages, high w/c: up to $10 \mu\text{m}$

7.2.2.3 Macropores

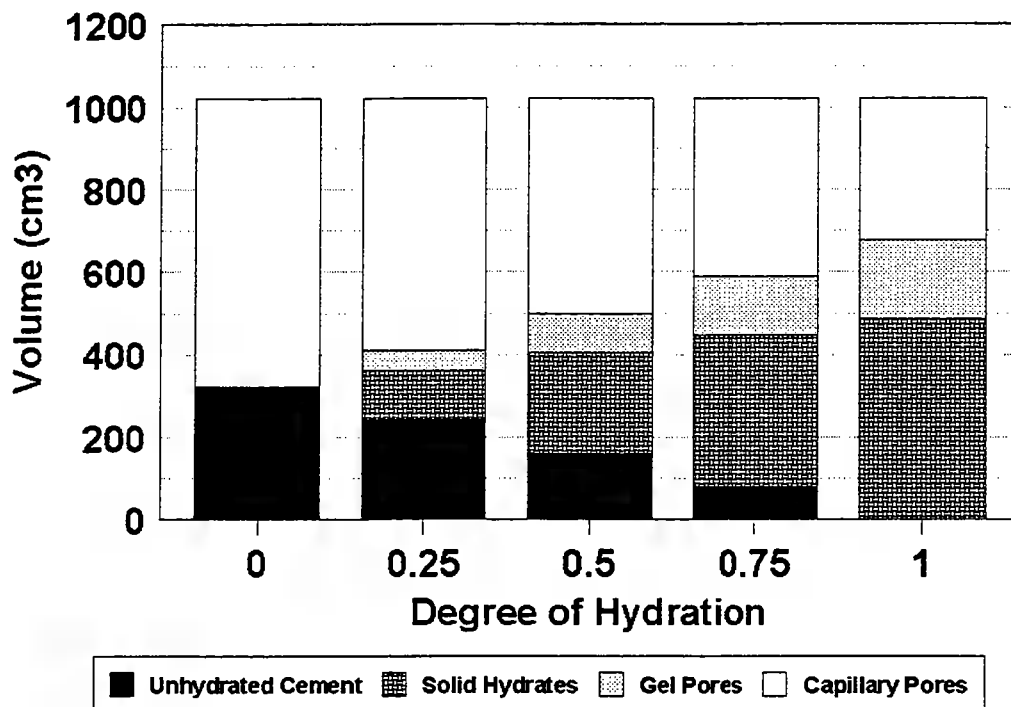
Air bubbles naturally entrapped or intentionally entrained during mixing (10 - $100 \mu\text{m}$).

"Compaction" voids: mm or cm

7.3 Evolution of pastes during hydration

Figures 16, 17 and 18 show the evolution of the structure of cement pastes, made with the same amount of cement (1 kg) but with different w/c ratios, during hydration (under water).

Figure 16: Development of Hydration of Cement Paste made with 1 kg of cement; w/c = 0.70



**Figure 17: Development of Hydration of Cement Paste made with 1 kg of cement;
w/c = 0.50**

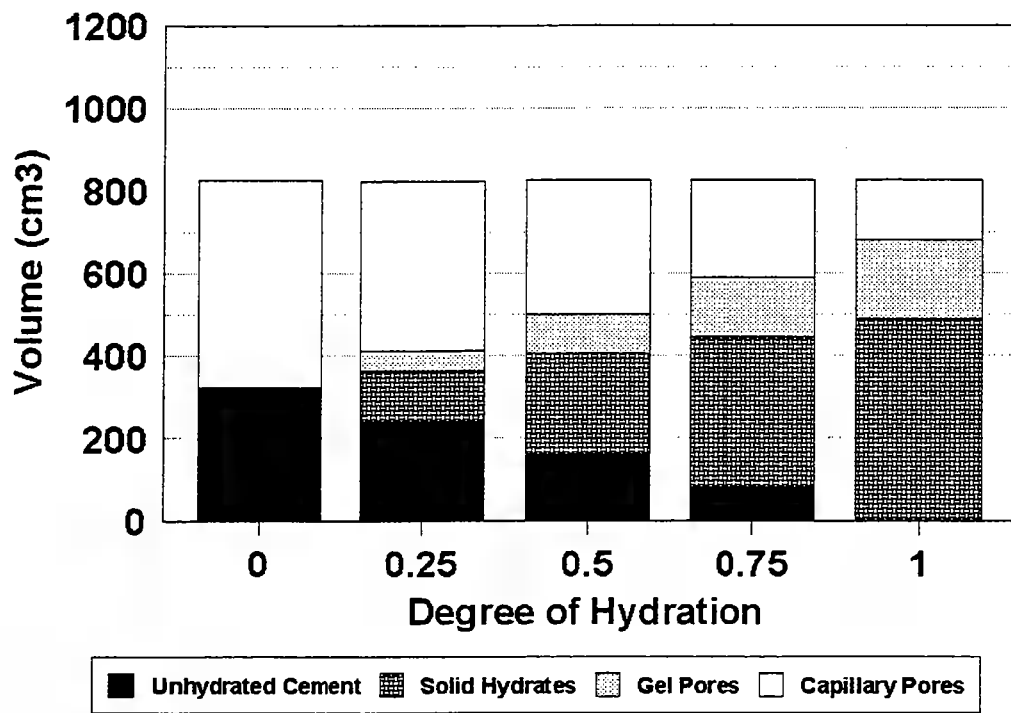
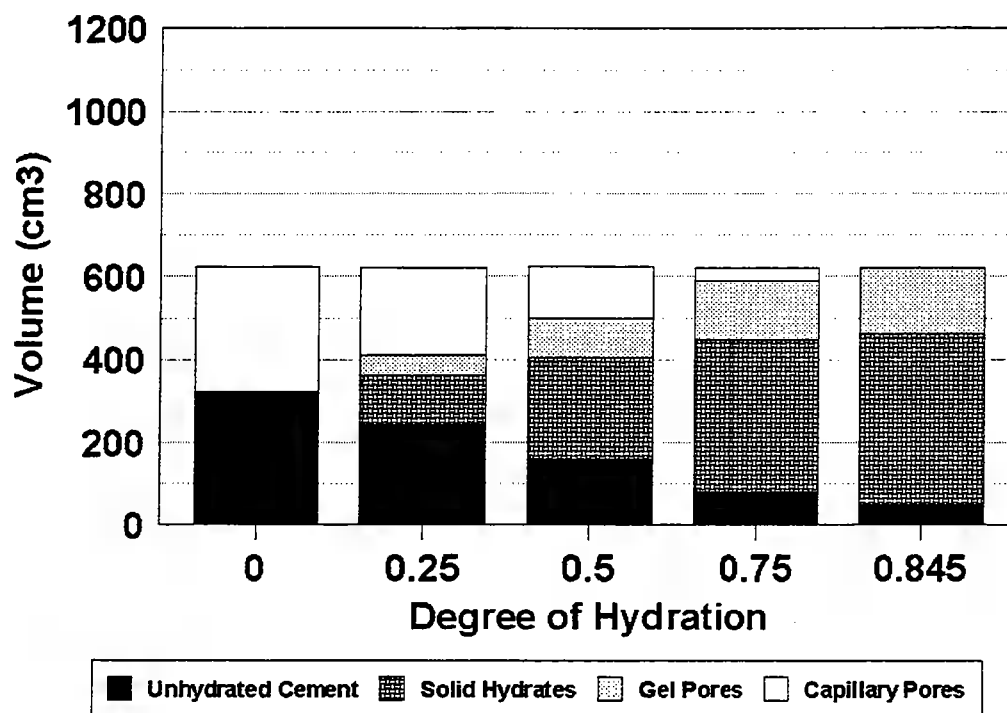


Figure 18: Development of Hydration of Cement Paste made with 1 kg of cement; w/c = 0.30



Initially, all pastes contain about 320 cm³ of unhydrated cement (1 kg), but different volumes of water, 700, 500 and 300 cm³ for w/c ratio 0.7, 0.5 and 0.3, respectively. Consequently, pastes with higher w/c ratio will have larger total volumes. The volume of water corresponds to the initial volume of capillary pores.

As hydration proceeds, the total volume remains basically constant, but the amount of unhydrated cement is gradually reduced. At degree of hydration 0.5, half of the original cement has been consumed and replaced by hydration products. The latter occupy a volume about double that of the original cement that hydrated, thus reducing the volume of capillary pores. From the total volume of hydrates, 72% are solid phase and 28% are gel pores.

If we compare the pastes with w/c 0.50 and 0.70 we see that, as they contained initially the same volume of cement, at any stage both pastes contain the same amount of hydration products. However, the paste with higher w/c ratio will contain more pores because the cement grains were more dispersed.

The paste with w/c ratio 0.30 can never reach full hydration because there is no room left to accommodate new hydration products. High-strength concretes, with very low w/c ratios always contain unhydrated cement for that reason.

Clearly, pastes and concretes with lower w/c ratios will have less and smaller capillary pores, thus explaining why they are stronger and less permeable (more durable), see Figures 19 and 20.

Figure 19: Strength vs. w/c-ratio

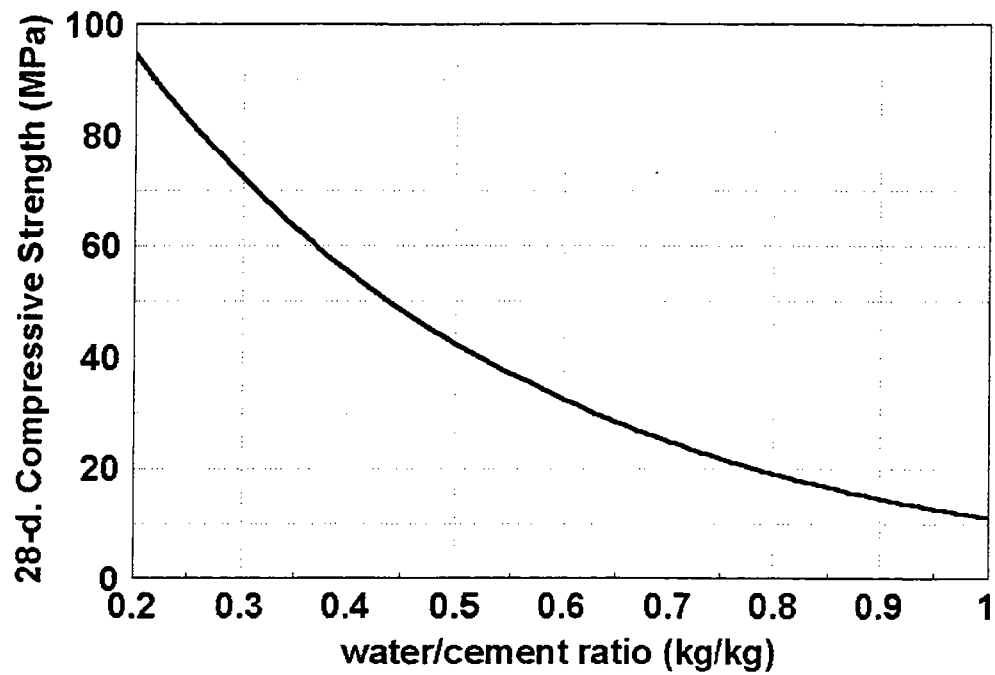
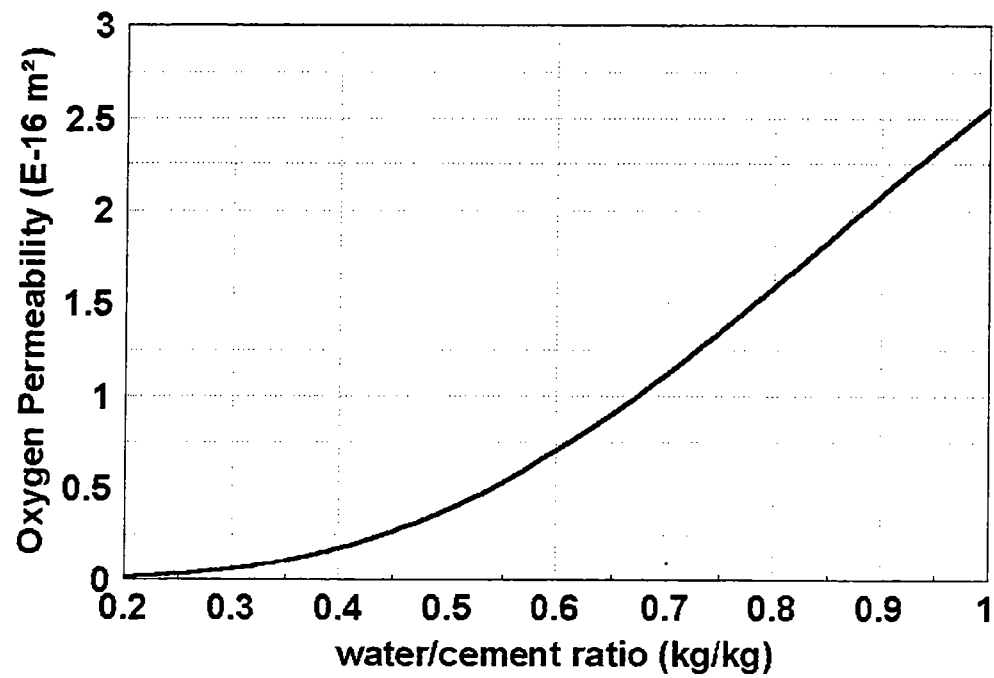


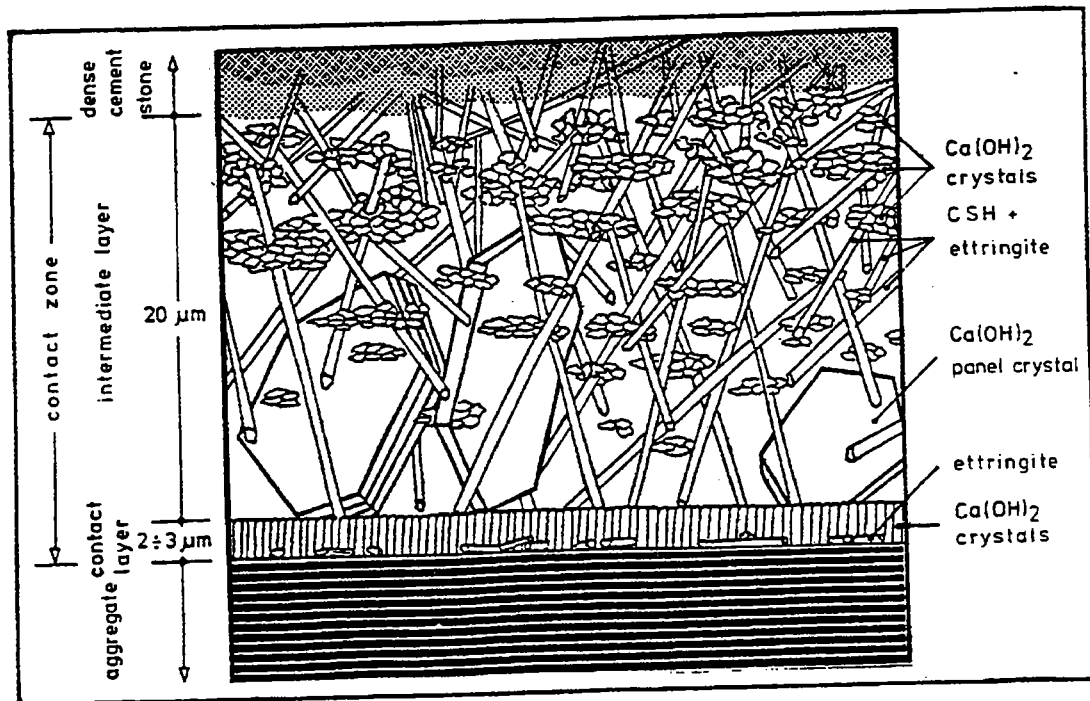
Figure 20: Permeability vs. w/c-ratio



7.4 Influence of the aggregates on the structure

Figure 21 shows that the presence of the aggregates distorts the structure of the HCP in their vicinity. In this contact or transition zone (about 20-25 μm thick), there exists a higher capillary porosity and a higher proportion of $\text{Ca}(\text{OH})_2$ than normal, making it weaker than the rest of the paste. This explains why, in the case of rounded and smooth aggregates the failure of concrete tends to happen at the interface between the coarse aggregate and the paste.

Figure 21: Model of the contact zone between cement stone and aggregate



To achieve high-strength concretes it is necessary to overcome this weakness of the contact zone. The increased porosity has to be compensated by using high dosages of a superplasticizer and the preferential alignment and presence of $\text{Ca}(\text{OH})_2$ crystals can be solved by adding microsilica or fly-ash.

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